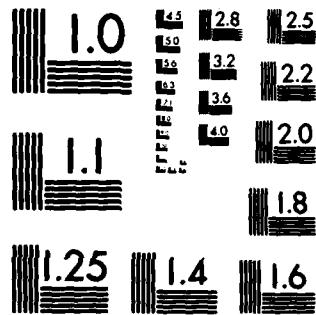


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ATOMIC AND SOLID STATE PHYSICS. J A STROSCIO ET AL.
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Dipole Active Surface Vibrational Resonances on Clean and
Hydrogen Covered Ni(110)

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Abstract:

A vibrational resonance of the surface metal atoms on the clean Ni(110) surface is observed by electron energy loss spectroscopy. The dipole coupling arises from the incomplete screening of the moving ion cores by the conduction electrons in the surface region. Surface lattice dynamical calculations are in excellent agreement with the measured spectra for the clean surface and show that there are no significant deviations in the surface force constant from the bulk value. This resonance results from a pseudo band gap in the longitudinal bulk phonon dispersion relation along the [110] direction. On the (1x2) reconstructed surface induced by hydrogen chemisorption, a dramatic decrease in intensity of the resonance is observed.



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I. Introduction

High resolution electron energy loss spectroscopy (EELS) has proven to be a powerful technique in the study of surface vibrations.¹ Recent refinements in this technique have led to the detection of surface phonon dispersions,² dipole active surface resonances,³ and dipole active bulk phonons.⁴ These measurements coupled with surface lattice dynamical calculations yield valuable information concerning the structure and interatomic forces in the surface region of clean and adsorbate covered surfaces, similar to the application of inelastic neutron scattering to the study of bulk phonon dispersions.

A primary interest is the effect of adsorbates on the interatomic forces at the surface. Recent surface phonon dispersion measurements on Ni(100) with a c(2×2) oxygen overlayer have indicated that the surface interlayer Ni force constant is reduced to 30% of the bulk value.^{5,6} In this paper we present results by EELS of dipole active surface vibrational resonances on clean and hydrogen covered Ni(110). From surface lattice dynamical calculations, the surface resonance is found to be a characteristic signature of the (110) surface of fcc metals and does not exist on the other low index (100) and (111) surfaces.³ Furthermore, an analysis of the experimental spectra for the clean and submonolayer hydrogen covered surfaces shows that there are no significant changes in the surface force constant from the bulk value. The adsorption of hydrogen at low temperatures on Ni(110) for coverages > 1 monolayer (ML) produces a hydrogen induced surface reconstruction with a (1×2) periodicity. EEL spectra on the reconstructed (1×2) surface show a drastic reduction in intensity of the surface resonance. Possible mechanisms for this effect are discussed.

The EEL spectra were recorded by a double pass 127° cylindrical deflector monochromator and analyzer. The spectrometer is housed in a multitechnique ultrahigh vacuum system with a base pressure of 4×10^{-11} Torr. The spectra were recorded in the specular direction with a resolution, full width at half maximum (FWHM), between 4 and 5 meV. The incidence angle with respect to the crystal normal direction is 60° and the acceptance angle of the analyzer is 1.8° (FWHM). The scattering plane containing the incident and scattered electrons is defined by the surface normal and the [110] crystal direction. The impact energy of the incident electrons was 4.3 eV. Hydrogen exposures were made using a microcapillary array doser. Coverage determination was obtained using thermal desorption spectroscopy (TDS) and calibrated against the observed (2x1)H and (1x2)H LEED patterns of which absolute coverages have been measured.⁷ Further information on the experimental arrangement and sample cleaning procedure is described in detail elsewhere.⁸

II. Surface Vibrational Resonance on Clean Ni(110)

Improved electron spectrometers operating with high resolution in the 3-5 meV range have given rise to rich structures in the energy loss spectrum below the maximum bulk phonon frequencies. Surface phonon vibrations on clean surfaces have been observed in off-specular measurements² which can probe the two-dimensional surface Brillouin zone and map out surface phonon branches which are outside the bulk manifolds. In dipole scattering, essentially the dipole active modes at the \bar{r} point in the surface Brillouin zone are probed. However, in the presence of a dipole active overlayer, metal surface phonons at points other than \bar{r} may be observed. When the unit cell of the adsorbate overlayer is different than the substrate surface layer, substrate surface phonons at points other than

the $\bar{\Gamma}$ point in the substrate surface Brillouin zone can be folded back into $\bar{\Gamma}$ and become dipole active by coupling to the motion of the adsorbed overlayer.⁹ In this case these vibrational modes are surface resonances since they couple to the bulk phonon bands and have a finite lifetime in the harmonic theory of lattice dynamics.¹⁰

Recently it has been shown that the incomplete screening by the conduction electrons in the surface region can give rise to an observable dynamic dipole moment of the metal layers.⁴ This mechanism thus allows surface vibrational modes to be observed on the clean surface without any indirect adsorbate coupling. Figure 1(a) shows the EEL spectrum of the clean Ni(110) surface. A sharp loss feature is observed at 24 meV. A similar loss feature at 20 meV has also been observed on the clean Cu(110) surface.³ Off-specular measurements show that these modes are dipole active. The ratio of the energies of these losses scales with the maximum phonon frequencies, which suggests that they are derived from bulk phonons propagating normal to the (110) surface.

The vibrational spectrum of inelastically scattered electrons from phonons at metal surfaces is directly related to the spectral function of dipole active displacements.¹¹ Surface lattice dynamics calculations have been performed using a transfer matrix technique for a semi-infinite surface and show that the sharp spectral feature at 24 meV for Ni(110) is a surface resonance which is derived from the dispersion of the longitudinal phonons propagating normal to the (110) surface.³ The physical origin behind this resonance lies in the unique geometrical structure of the fcc (110) surface.

The dispersion of phonons propagation along the [110] direction is illustrated in Fig. 2. The solid line results from a simple one parameter

nearest neighbor central force constant model used in the lattice dynamical calculations. It is seen that this model gives an accurate description of the phonon dispersion measured by inelastic neutron scattering.¹² As observed in Fig. 2 this dispersion is characterized by a local maximum well within the Brillouin zone. This maximum results directly from the fact that an atom in a layer normal to the [110] direction has nearest neighbors in both the first and second neighboring layers (see inset in Fig. 2). The stationary points in the phonon dispersion give rise to characteristic Van Hove singularities in the density of states projected on the bulk layers as shown by the dashed curve in Fig. 3. These singularities disappear in the projected density of states on the surface layer due to destructive interference between incident and reflected phonons from the surface. On the (110) surface there is a pseudo band gap for energies between 0 and 26 meV as seen from the strong depletion in the projected bulk density of states given in Fig. 3. For an absolute band gap the surface can split off a localized mode from the band into the gap. The low density of states in the pseudo band gap turns this mode into a resonance as shown in Fig. 3. The best agreement with the experimental spectrum in Fig. 1(a) is obtained with the interlayer surface force constant taken to be equal to the bulk value, indicating that there is no significant stiffening or softening of the surface force constants on the clean Ni(110) surface.

III. Effect of Hydrogen Chemisorption on the (110) Surface Resonance

The adsorption of hydrogen on Ni(110) has been a subject of many recent investigations. Taylor and Estrup reported to observe a faint (2x1) LEED pattern after hydrogen adsorption at low temperatures.¹³ At higher exposures this pattern transformed into a (1x2) phase with intense half

order beams indicating a distortion in the substrate layer. Recent He diffraction¹⁴ and video-LEED¹⁵ experiments have shown that for coverages below one monolayer (ML) a sequence of hydrogen ordered phases is observed, in particular, a (2x1) ordered hydrogen phase occurs at $\theta = 1$ ML. Above $\theta = 1$ ML, reconstructed (1x2) domains grow in at the expense of the (2x1) phase until saturation coverage is reached at $\theta = 1.5$ ML. Results from He diffraction experiments, which are consistent with LEED observations, suggest that in the 2x1 phase hydrogen atoms occupy low symmetry bridge sites near the threefold sites along the [110] rows and form a zig-zag arrangement. On the reconstructed (1x2) surface a model has been proposed, involving pairing of alternate [110] rows with the additional H bonded to the second layer Ni atoms.

Figures 1(b) and 1(c) show the vibrational spectra of the (2x1) and (1x2) surfaces. Two hydrogen losses are observed at 79 and 130 meV for the (2x1) surface, and 77 and 114 meV for the (1x2) reconstructed surface. These loss features are in agreement with previous EEL measurements on this system.¹⁶⁻¹⁸ While assignments of these modes have varied, recent theoretical studies¹⁹⁻²² would suggest that the high frequency modes at 130 and 114 meV are to be attributed to the perpendicular Ni-H stretch mode (which makes an angle with the [110] surface normal) for H atoms in the low symmetry bridge site shifted towards the three-fold coordination of the (111) microfacets along the [110] rows. The lower frequency modes are assigned to the in plane bending vibration since two dipole active modes are expected for the C₃ symmetry of this adsorption site. Previous off-specular experiments¹⁶ reported the observation of an additional mode at 140 meV on the reconstructed surface which could be attributed to H atoms bonded to second layer Ni atoms.

Focusing on the low frequency portion of the EEL spectra in Figs. 1(a) and 1(b), the surface vibrational resonance is seen not to be influenced by the presence of the (2x1) hydrogen overlayer. Due to the low mass of the hydrogen atoms they can essentially only influence the motion of the substrate atoms by changing the substrate force constants. This observation shows that the bonding of the hydrogen atoms in the (2x1) phase has no dramatic effect on the bonding between the substrate metal atoms.

For the reconstructed surface the surface resonance has disappeared from the EEL spectra in Fig. 1(c). This is clearly seen in Fig. 1(b) where for comparison a portion of the spectrum for the reconstructed surface is shown by a dashed curve. Figure 4(a) shows the inelastic intensity above the background of the surface resonance as a function of hydrogen coverage. The intensity is relatively constant for $\theta < 1$ ML on the unreconstructed surface. For coverages greater than 1 ML a rapid decrease in intensity is observed. Observation by LEED of a coexistence of (2x1) and (1x2) domains for $\theta > 1$ ML suggests that the resonance intensity is proportional to the fraction of unreconstructed surface in the (2x1) hydrogen phase which is depleted as the coverage increases to form the reconstructed (1x2) phase. A similar relation is seen in the coverage dependence of the half order beam intensity in the (2x1) phase from LEED measurements.¹⁵

A reconstruction of the surface metal atoms results in a surface unit cell that is different than the underlying substrate layer and will introduce, in general, a new set of vibrational modes. As indicated in Section II, this makes it possible for the resonance to couple to modes at points other than the \bar{r} point of the substrate surface Brillouin zone. These effects could lead to a broad distribution of inelastic intensity

which cannot be distinguished from the background and hence account for the observed spectral distribution in Fig. 1(c).

Alternately, the disappearance of the resonance could be due to a redistribution of spectral intensity to lower energies below the tail of the instrumentally broadened elastic peak. This can be seen to result from a weakening of the surface force constants during the reconstruction. By invoking spectral sum rules, a redistribution of the spectral intensity to lower energies can be shown to occur if the restoring force for dipole active displacements of the substrate atoms is decreased.¹¹ This assertion is illustrated by the calculated vibrational density of states of the unreconstructed surface in Fig. 3 for different values of the surface force constant K_S . A decrease in K_S causes the surface resonance to broaden and shift to lower energies. As seen in Fig. 3, a 50% reduction in K_S is sufficient to account for the disappearance of the surface resonance. Such a large reduction is not unreasonable and can be compared to a 70% reduction obtained for an oxygen overlayer on Ni(100).^{5,6} However, a definitive conclusion on which effects actually cause the observed reduction of the surface resonance cannot be reached since a detailed analysis based on surface lattice dynamical calculations is prohibited by the fact that the structure of the reconstructed surface has not been determined.

In summary, the long range electron-phonon coupling due to incomplete screening by the conduction electrons in the surface region allows surface vibrations of the metal atoms to be observed by EELS. In particular, the Ni(110) surface is characterized by a vibrational resonance at 24 meV. Surface lattice dynamical calculations are in agreement with experimental results from the clean and submonolayer hydrogen covered surfaces with the

surface force constant remaining the same as the bulk value. On the (1x2) reconstructed surface formed by hydrogen chemisorption an extinction of the resonance is observed. Further experiments on this system are needed to elucidate fully the mechanisms for this effect.

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Figure Captions

- Fig. 1. Electron energy loss spectra of : (a) clean Ni(110) at 300 K showing the surface resonance at 24 meV, (b) 1 ML H on Ni(110) at 80 K forming a (2×1) overlayer structure, (c) 1.5 ML H on Ni(110) at 80 K forming a reconstructed (1×2) structure. All spectra were recorded in the specular direction. For comparison, a portion of the spectrum in (c) is drawn in (b), dashed curve.
- Fig. 2. Nickel bulk phonon dispersion along the [110] direction. The solid line shows the calculated dispersion for longitudinal phonons and is compared with measurements by inelastic neutron scattering (□) from Ref. 12. The inset shows the side view, perpendicular to the [110] direction, of the atomic arrangement for the fcc (110) surface.
- Fig. 3. Vibrational density of states for longitudinal phonons given in Fig. 2 projected on the dipole active displacements (solid line) for different ratios of the interlayer force constant K_s relative to the bulk value K_b . These dipole active displacements are modelled by the relative motion of the two outermost surface layers. The dashed line shows the projected density of states on the relative displacement of two neighboring bulk layers.
- Fig. 4. EEL intensity above the background of the surface vibrational resonance at 24 meV normalized to the elastic intensity for various initial hydrogen coverages.

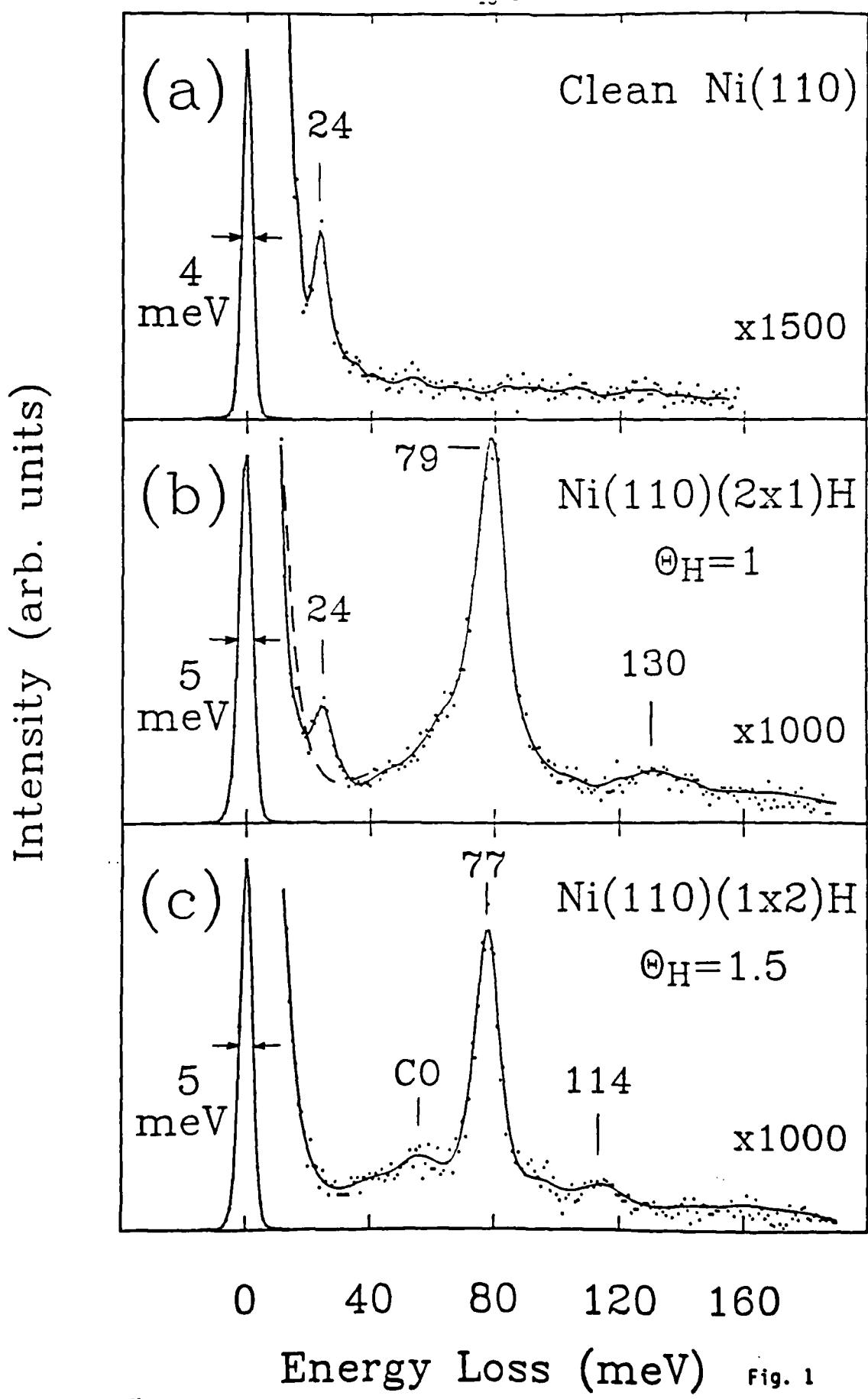


Fig. 1

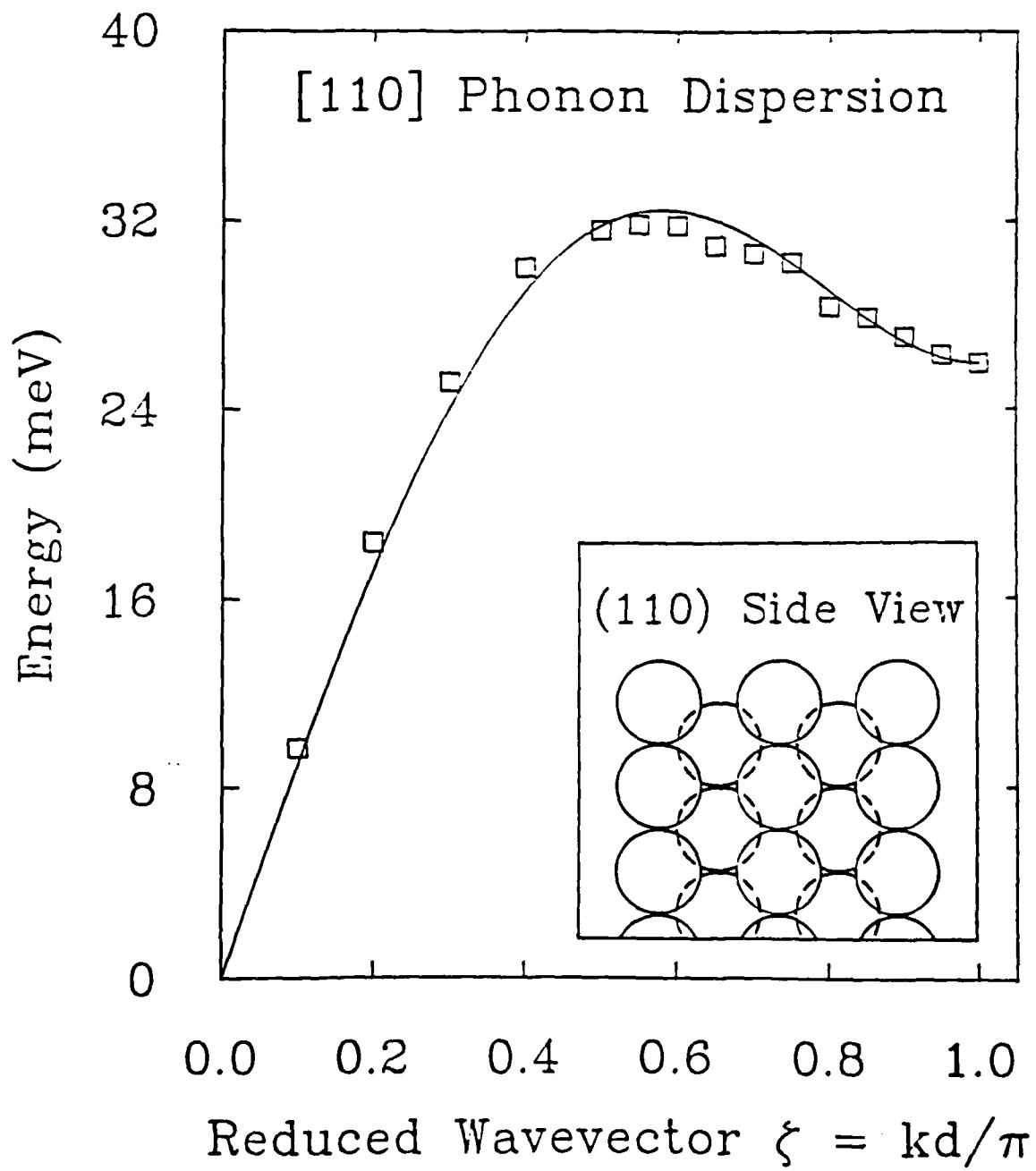


Fig. 2

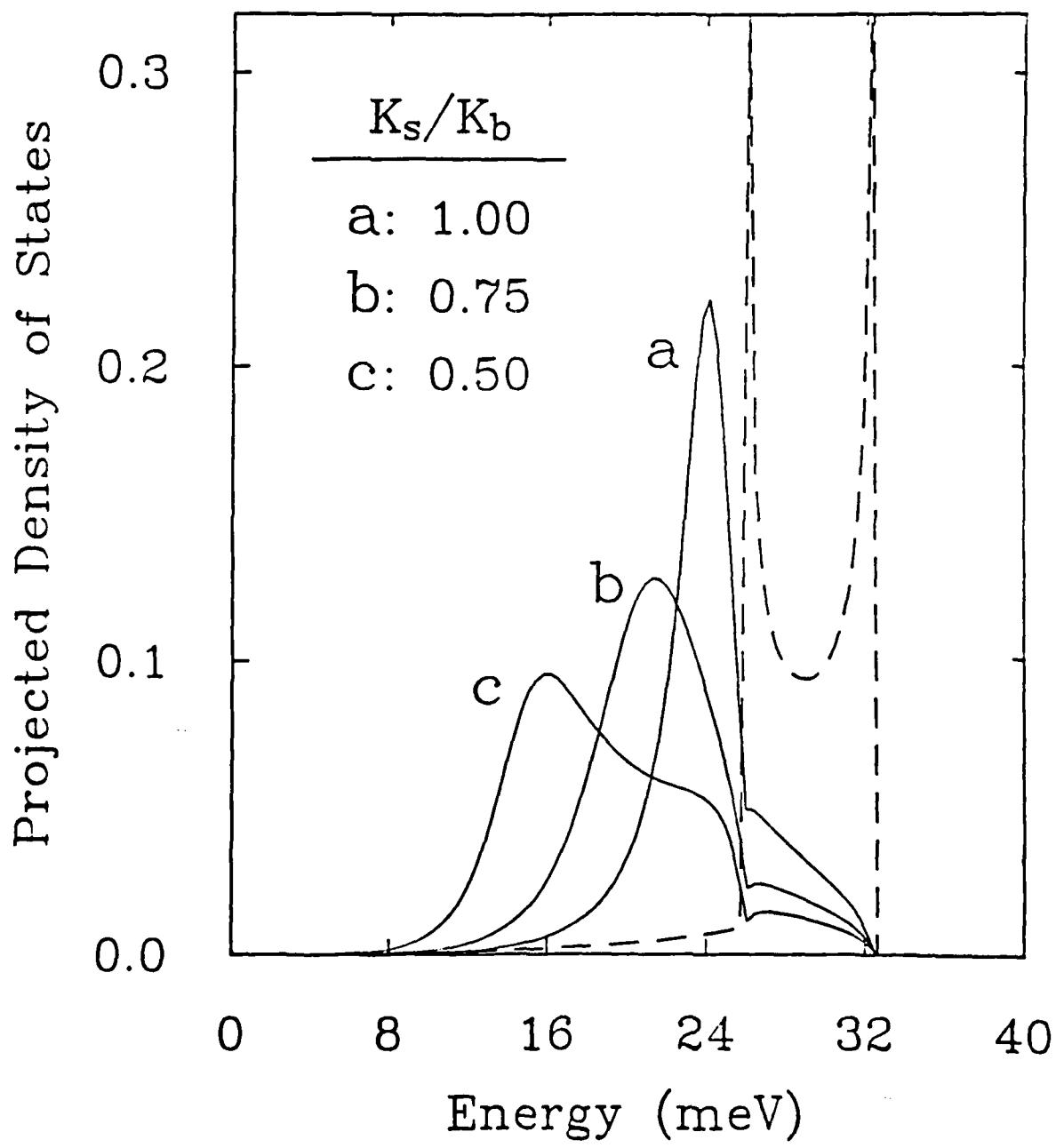


Fig. 3

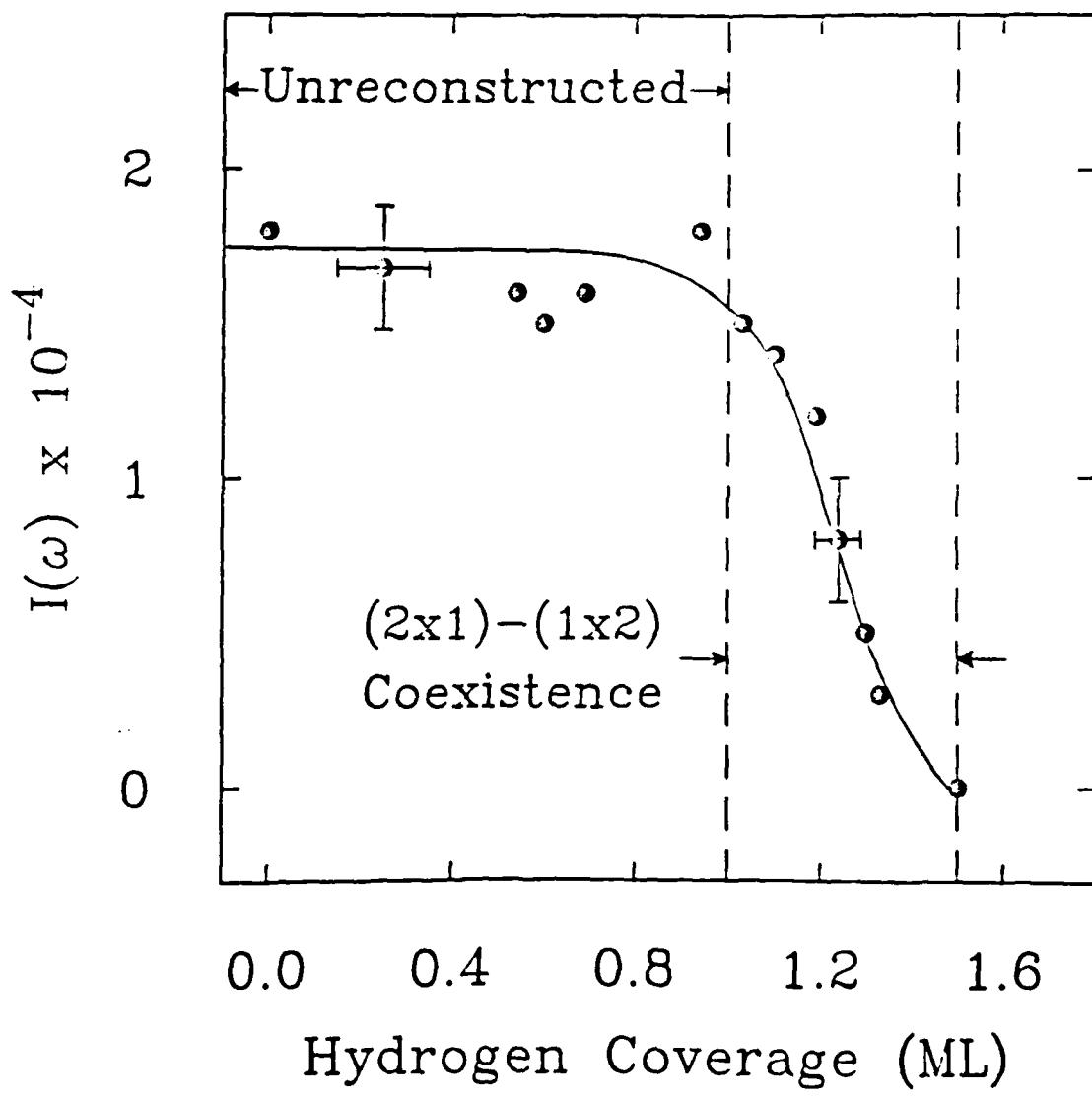


Fig. 4

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